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Thermodynamic and thermoacoustical parameters of pure liquids at elevated pressures

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Abstract : Thermodynamic and thermoacoustical parameters are deduced theoretically for nine liquids at elevated pressures, using experimental viscosity, density and ultrasonic velocity data available in literature. The theoretical treatment provides a method for establishing relationship between various parameters and gives satisfactory qualitative and quantitative descriptions of various properties of liquids.

Keywords : Thermodynamic and thermoacoustical parameters, pure liquids, elevated pressures

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Measurement of the sound velocity offers a convenient method for determining certain thermodynamic properties of liquids not easily obtained by other means. An extensive work has been done for investigating the liquid state through the analysis of ultrasonic propagation parameters, but comparatively lesser work has been carried out in the recent past [1–3], to correlate ultrasonic velocity with other physical and thermodynamic properties of liquid state theories. Some important correlations with other auxiliary parameters such as internal pressure (P_{in}), Grüneisen parameter (Γ), energy of vaporization (ΔU_{vap}), heat of vaporization (ΔH_{vap}), cohesive energy density (ced) and solubility parameter (δ) can very well be studied by the measurement of ultrasonic velocity (c), viscosity (η) and density (ρ).

The present paper deals with the evaluation of the above mentioned parameters at elevated pressures. Various liquids considered for the present investigation are water, methyl alcohol, ethyl alcohol, n-propyl alcohol, n-butyl alcohol, eugenol, carbontetrachloride, toluene and n-hexane. The experimental data of the sound velocity

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and related properties utilized in the present calculations weɛe collected from different sources [4,5].

Internal pressure has been studied by Hildebrand and Scott [6,7] and subsequently by several coworkers [8–11]. The method proposed by Suryanarayana [12], has been utilized to obtain the internal pressure as,

$$P_{int} = bRT.\ (k\eta/c)^{1/2}.\ \left(p^{2/3}/M^{7/6}\right), \tag{1}$$

where b is the packing factor K is a dimensionless constant independent of temperature having a value of 4.28×10^9, M is the molecular weight and b is equal to 1.78 for close packed hexagonal structure [12]. The other symbols have their usual meaning.

Pseudo Grüneisen parameter (Γ) is an important quantity in studying the internal structure, molecular order and other themoacoustic properties of liquids [13–15] and polymers [16]. Following relation between Pseudo Grüneisen parameter and internal pressure has been derived by Sharma :

$$\Gamma = (V/3RT) \cdot P_{int}. \tag{2}$$

From eqs. (1) and (2) we obtain the relationship for the Grüneisen parameter as

$$\Gamma = b/3\{K\eta/C\}^{1/2} \cdot \left\{V^{1/3}/M^{1/2}\right\}, \tag{3}$$

where V is the molar volume calculated by the relation $V = M/p$. The energy of vaporization, ΔU_{vap} may be obtained by the relation :

$$\Delta U_{vap} = P_{int} \cdot V. \tag{4}$$

Further, the heat of vaporization $(\Delta H)_{vap}$ may be calculated using the value of energy of vaporization according to

$$\Delta H_{vap} = \Delta U_{vap} + RT. \tag{5}$$

The cohesive energy density (ced) is given by,

$$\text{ced} = n(\Delta U_{vap}/V) = (\Delta U_{vap}/V). \tag{6}$$

Since the quantity 'n' approaches unity for nonpolar liquids,

δ is simply the square root of cohesive energy density :

$$\delta = \sqrt{\text{ced}}. \tag{7}$$

Further, ultrasonic velocity has been utilized to study other related parameters like molar sound velocity (R), molar compressibility (W) and acoustic impedance (Z).

The molar sound velocity (R) of the liquid has been defined by the relation

$$R = (M/\rho)\, C^{1/3}. \tag{8}$$

Similarly the molar compressibility (W) can be expressed as

$$W = (M/\rho)\,K_s^{-1/7}. \tag{9}$$

Here, K_s is the adiabatic compressibility, obtained by the expression

$$K_s = 1/C^2\rho. \tag{10}$$

Acoustic impedance (Z) has been given by the relations

$$Z = \rho c. \tag{11}$$

Different parameters thus obtained in the entire pressure range 1–1000 kg cm^{-2} (for toluene and n-hexane) and 1–5000 kg cm^{-2} (for rest of the liquids), have been shown in Tables 1 to 9. The liquids undertaken for the present investigation are water, methyl alcohol, ethyl alcohol, n-propyl alcohol, n-butyl alcohol, eugenol, carbontetrachloride, n-hexane and toluene. Density (ρ), ultrasonic velocity (c) and viscosity (η) values at elevated pressures and at temperature 303 K are recorded in Tables 1 to 9. However, in the case of water, n-propyl alcohol and carbontetrachloride the data are available at different temperatures. For all the liquids the ultrasonic velocity is almost double as the pressure increases from 1 to 10000 Kg cm^{-2}.

Table 1. Thermodynamic parameters of water at elevated pressures at different temperatures.

P (Kg cm^{-2})	ρ (Kg m^{-3})	c (m s^{-1})	$\eta \times 10^3$ (N s m^{-2})	Pin (atm)	Γ	ΔU (J mole^{-1})	ΔH (J mole^{-1})	ced $\times 10^{-6}$ (J/m^3)	$\delta \times 10^{-3}$ (J/m^3)$^{1/2}$
				T = 273 K					
1.00	1000.00	1406.00	1.79	31896.76	8.55	58226.89	60496.69	3231.24	56.84
246.00	1010.00	1439.00	1.72	31111.96	8.26	56226.95	58496.75	3151.74	56.14
852.00	1040.00	1558.00	1.65	29862.52	7.70	52426.07	54695.87	3025.16	55.00
1669.00	1070.00	1700.00	1.68	29398.96	7.37	50152.94	52422.74	2978.20	54.57
3238.00	1120.00	1953.00	1.86	29752.95	7.12	48496.27	50766.07	3014.06	54.90
4724.00	1160.00	2155.00	2.14	31100.54	7.19	48928.47	51198.27	3150.58	56.13
				T = 283.3 K					
1.00	1000.00	1453.00	1.40	28795.71	7.45	52565.99	54921.43	2917.09	54.01
521.00	1020.00	1540.00	1.35	27831.50	7.06	49819.05	52174.49	2819.41	53.10
1907.00	1070.00	1769.00	1.35	26809.50	6.48	45735.47	48090.91	2715.88	52.11
4008.00	1130.00	2076.00	1.51	27142.95	6.21	43857.11	46212.55	2749.66	52.44
				T = 303K					
1.00	1000.00	1510.00	0.87	23815.72	5.75	43475.13	45994.36	2412.60	49.12
228.00	1000.00	1556.00	0.88	23595.50	5.70	43073.11	45592.34	2390.29	48.89
1017.00	1040.00	1687.00	0.92	23783.98	5.53	41754.71	44273.94	2409.39	49.09
3001.00	1100.00	1982.00	1.07	24565.63	5.39	40762.80	43282.03	2488.57	49.89

Table 2. Thermodynamic parameters of methyl alcohol at elevated pressures and temperature 303 K.

P (Kg cm^{-2})	ρ (Kg m^{-3})	c (m s^{-1})	$\eta \times 10^3$ (N s m^{-2})	Pin (atm)	Γ	ΔU (J mole^{-1})	ΔH (J mole^{-1})	ced $\times 10^{-6}$ (J/m^3)	$\delta \times 10^{-3}$ (J/m^3)$^{1/2}$
1 00	782 00	1094.00	0 51	9292.29	5.10	38566.57	41085.80	941.34	30.64
232 00	802.00	1216.00	0 57	9476.08	5.08	38350.21	40869.44	959.96	30.98
1023.00	849 00	1518.00	0.75	10105.12	5.11	38633.66	41152.89	1023.68	31.99
2007.00	885.00	1761.00	0.98	11025.65	5.35	40432 90	42952.13	1116.93	33.42
3019.00	916.00	1979 00	1.23	11922.53	5.59	42248.43	44767.66	1207.79	34.75
4211 00	947 00	2178 00	1 56	13086 05	5.94	44846.94	47366.17	1325.66	36 41

Table 3. Thermodynamic parameters of ethyl alcohol at elevated pressures and temperature 303 K.

P (Kg cm^{-2})	ρ (Kg m^{-3})	c (m s^{-1})	$\eta \times 10^3$ (N s m^{-2})	Pin (atm)	Γ	ΔU (J mole^{-1})	ΔH (J mole^{-1})	ced $\times 10^{-6}$ (J/m^3)	$\delta \times 10^{-3}$ (J/m^3)$^{1/2}$
1.00	781.00	1115 00	1.00	8429.63	6.67	50374.34	52893 57	853.95	29 22
246.00	800.00	1256.00	1.14	8617 14	6.65	50272 72	52791.95	872.94	29 55
1036.00	848.00	1578.00	1.62	9527.52	6 93	52340 98	54860.21	965.17	31.07
3130.00	915.00	2074.00	3 24	12364 05	8 35	63064 17	65583.40	1252.52	35.39
4882.00	957 00	2361.00	5.12	15009 76	9 69	73198.48	75717.71	1520.53	38.99

Table 4. Thermodynamic parameters of n-propyl alcohol at elevated pressures at different temperatures.

P (Kg cm^{-2})	ρ (Kg m^{-3})	c (m s^{-1})	$\eta \times 10^3$ (N s m^{-2})	Pin (atm)	Γ	ΔU (J mole^{-1})	ΔH (J mole^{-1})	ced $\times 10^{-6}$ (J/m^3)	$\delta \times 10^{-3}$ (J/m^3)$^{1/2}$
				T = 296.2 K					
1.00	804.00	1220.00	2.18	8703 76	8.92	65864.25	68326.95	881 72	29.69
				T = 325 K					
1.00	779.00	1114.00	1.01	6660.84	6.42	52017.51	54719.66	674.76	25.98
				T = 303 K					
1.00	798 00	1190.00	1.72	7967.79	8.04	60746.97	63266.20	807.16	28.41
539.00	834.00	1457.00	2.49	8922.63	8.61	65089.03	67608.26	903.89	30.06
1000.00	857.00	1624.00	3.29	9892.46	9.29	70229.67	72748.90	1002 14	31.66
1963.00	889.00	1878.00	5.30	11964.74	10.84	81887.07	84406.30	1212.06	34.81
5031.00	958.00	2431.00	17.28	19958.83	16.77	126752.26	129271.49	2021.89	44.97

Table 4. *(Cont'd.)*

P (Kg cm^{-2})	ρ (Kg m^{-3})	c (m s^{-1})	$\eta \times 10^3$ (N s m^{-2})	Pin (atm)	Γ	ΔU (J mole^{-1})	ΔH (J mole^{-1})	ced $\times 10^{-6}$ (J/m^3)	$\delta \times 10^{-3}$ (J/m^3)$^{1/2}$
				T = 348 K					
1.00	760.00	1052.00	0.68	5923.85	5.46	47426.23	50319.60	600.10	24.50
961.00	827.00	1517.00	1.28	7160.30	6.07	52675.63	55569.00	725.36	26.93
2072.00	873.00	1843.00	2.11	8647.09	6.94	60267.17	63160.54	875.98	29.60
3106.00	906.00	2063.00	3.05	10072.43	7.79	67589.17	70482.54	1020.37	31.94
4381.00	919.00	2300.00	4.45	11632.55	8.87	77009.27	79902.64	1178.41	34.33

Table 5. Thermodynamic parameters of *n*-butyl alcohol at elevated pressures and temperature 303 K.

P (Kg cm^{-2})	ρ (Kg m^{-3})	c (m s^{-1})	$\eta \times 10^3$ (N s m^{-2})	Pin (atm)	Γ	ΔU (J mole^{-1})	ΔH (J mole^{-1})	ced $\times 10^{-6}$ (J/m^3)	$\delta \times 10^{-3}$ (J/m^3)$^{1/2}$
1.00	800.00	1234.00	2.30	7090.73	8.81	66551.67	69070.90	718.31	26.80
512.00	837.00	1469.00	3.32	8046.99	9.55	72184.54	74703.77	815.18	28.55
1998.00	900.00	1905.00	8.24	11684.30	12.90	97485.79	100005.02	1183.65	34.40
4023.00	955.00	2283.00	20.03	17312.03	18.01	136109.36	138628.59	1753.76	41.88
4983.00	976.00	2428.00	30.32	20955.52	21.33	161209.73	163728.96	2122.86	46.07

Table 6. Thermodynamic parameters of eugenol at elevated pressures and temperature 303 K.

P (Kg cm^{-2})	ρ (Kg m^{-3})	c (m s^{-1})	$\eta \times 10^3$ (N s m^{-2})	Pin (atm)	Γ	ΔU (J mole^{-1})	ΔH (J mole^{-1})	ced $\times 10^{-6}$ (J/m^3)	$\delta \times 10^{-3}$ (J/m^3)$^{1/2}$
1.00	1058.00	1482.00	6.20	5060.24	10.53	79553.06	82072.29	512.62	22.64
354.00	1080.00	1603.00	9.80	6201.61	12.64	95517.80	98037.03	628.24	25.06
836.00	1099.00	1742.00	17.70	8088.53	16.20	122425.44	124944.67	819.39	28.63
1479.00	1119.00	1890.00	38.90	11651.25	22.92	173198.23	175717.46	1180.31	34.36
2366.00	1141.00	2062.00	121.00	19930.31	38.45	290554.37	293073.60	2019.00	44.93
3559.00	1169.00	2273.00	596.00	42816.23	80.63	609232.98	611752.21	4337.41	65.86
3895.00	1172.00	2307.00	1027.00	55884.13	104.97	793138.36	795657.59	5661.23	75.24

Table 7. Thermodynamic parameters of carbontetrachloride at ele [illegible] and different temperatures.

(Kg cm^{-2})	ρ (Kg m^{-3})	c (m s^{-1})	$\eta \times 10^3$ (N s m^{-2})	Pin (atm)	Γ	ΔU (J mole^{-1})	ΔH (J mole^{-1})	ced $\times 10^{-6}$ (J/m^3)	$\delta \times 10^{-3}$ (J/m^3)$^{1/2}$
				T = 303 K					
1.00	1570.00	907.00	0.84	3342.74	4.39	33175.55	35694.78	338.63	18.40
398.00	1630.00	1045.00	1.20	3816.43	4.83	36484.98	39004.21	386.62	19.66
820.00	1670.00	1163.00	1.68	4350.20	5.37	40591.81	43111.04	440.69	20.99
1496.00	1730.00	1323.00	2.62	5214.77	6.22	46968.64	49487.87	528.27	22.98
				T = 348 K					
1.00	1510.00	770.00	0.48	3069.00	4.13	35799.17	38692.54	351.42	18.75
342.00	1550.00	923.00	0.66	3344.74	4.39	38132.20	41025.57	384.24	19.60
809.00	1620.00	1066.00	0.93	3804.90	4.78	41495.16	44388.53	437.02	20.91
1464.00	1670.00	1222.00	1.39	4433.56	5.28	45843.30	48736.67	497.70	22.31
2942.00	1780.00	1470.00	2.40	5542.39	6.24	54167.23	57060.60	626.86	25.04

Table 8. Thermodynamic parameters of n-hexane at elevated pressures and temperature 303 K.

P (Kg cm^{-2})	ρ (Kg m^{-3})	c (m s^{-1})	$\eta \times 10^3$ (N s m^{-2})	Pin (atm)	Γ	ΔU (J mole^{-1})	ΔH (J mole^{-1})	ced $\times 10^{-6}$ (J/m^3)	$\delta \times 10^{-3}$ (J/m^3)$^{1/2}$
1.00	651.00	1060.00	0.29	1986.00	3.52	26633.17	29152.40	201.19	14.18
1000.00	721.00	1584.00	0.63	2563.27	4.11	31037.99	33557.22	259.67	16.11
4000.00	810.00	2310.00	2.40	4477.14	6.39	48252.99	50772.22	453.55	21.30
8000.00	880.00	2890.00	9.57	8447.09	11.09	83800.20	86319.43	855.72	29.25
10000.00	894.00	3110.00	18.60	11472.18	14.83	112032.87	114552.10	1162.17	34.09

Table 9. Thermodynamic parameters of toluene at elevated pressures and temperature 303 K.

P (Kg cm^{-2})	ρ (Kg m^{-3})	c (m s^{-1})	$\eta \times 10^3$ (N s m^{-2})	Pin (atm)	Γ	ΔU (J mole^{-1})	ΔH (J mole^{-1})	ced $\times 10^{-6}$ (J/m^3)	$\delta \times 10^{-3}$ (J/m^3)$^{1/2}$
1.00	857.00	1290.00	0.52	2678.23	3.86	29168.86	31688.09	271.31	16.47
1000.00	910.00	1680.00	0.98	3353.31	4.55	34394.65	36913.88	339.70	18.43
4000.00	980.00	2265.00	4.03	6153.04	7.76	58604.72	61123.95	623.32	24.97
8000.00	1030.00	2785.00	26.20	14625.71	17.54	132546.50	135065.73	1481.63	38.49
10000.00	1040.00	2995.00	80.50	24881.47	29.55	223322.25	225841.48	2520.57	50.21

The values of internal pressure increase gradually with increase in pressure at temperature 303 K and above whereas below 303 K, the internal pressure decreases with increase in pressure as in the case of water. The values of pseudo Grüneisen parameter, energy of vaporization, heat of vaporizations, cohesive energy density and solubility parameter show an increase with increase in pressure. However, reverse trend has been found in the case of water where all the above mentioned parameters show a decrease with increase in pressure. The values of molar sound velocity (R), and molar compressibility (W) calculated by eqs. (8) and (9) respectively are plotted against pressure. Linear plots are obtained as shown in Figures 1, 2.

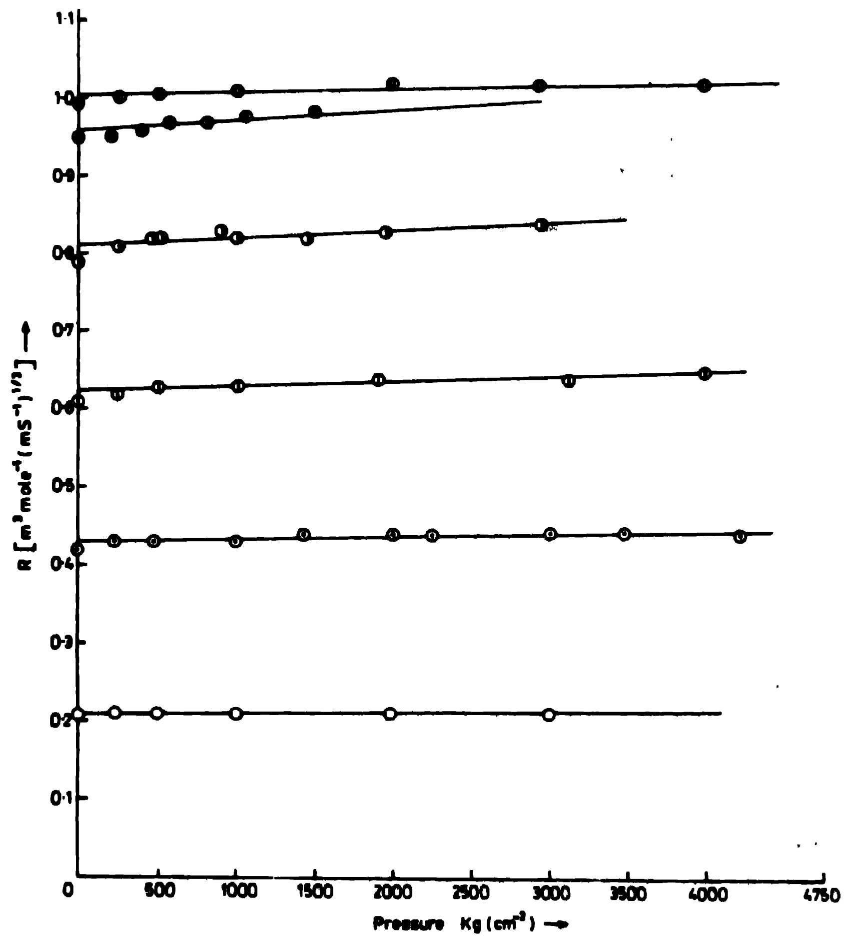

Figure 1. Molar sound velocity of pure liquids at high pressures and temperature 303 K : O water, ⊖ methyl alcohol, ◐ ethyl alcohol, O n-propyl alcohol, ● n-butyl alcohol and ● carbon-tetrachloride.

The present investigation suggests convenient means for establishing relationship between different parameters. To conclude, it may be claimed that the Suryanarayana's [12] expression can be successfully used to obtain the internal pressure of pure liquids. This approach offers a simple method to describe liquid state properties relating to the sound propagation data.

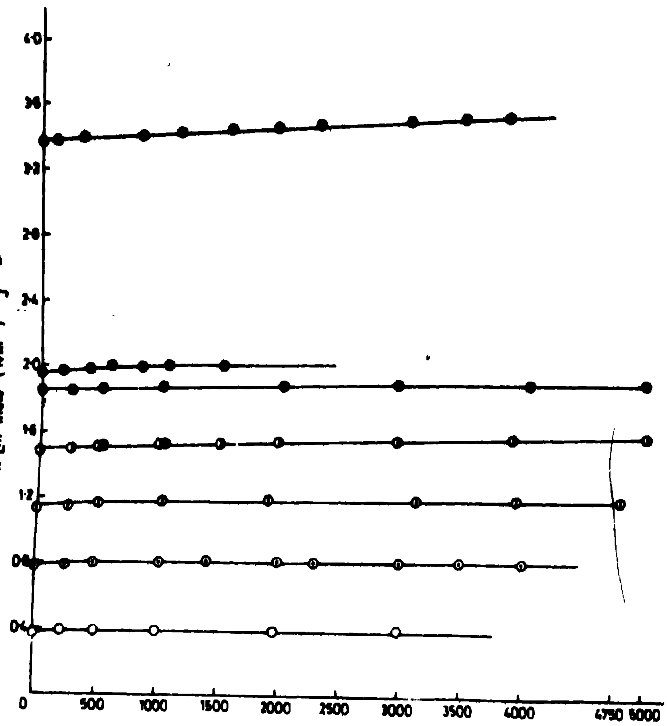

Figure 2. Molar compressibility of pure liquids of high pressures and temperature 303 K : O water, ⊕ methyl alcohol, ● ethyl alcohol, ◑ n-propyl alcohol, ● butyl alcohol, ⊗ carbon-tetrachloride and O eugenol.

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